

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Thomas KOTHE, et al. Docket No.: COZ-0535
Serial No. 10/584,869 Examiner: Angela C. SCOTT
371 Date: April 20, 2007 Group Art Unit: 1796
Title: SETTABLE COMPOSITION CONTAINING LIME, A CEMENTITIOUS
COMPOSITION AND A POLYMER

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APPELLANTS' BRIEF UNDER 37 C.F.R. § 41.37

To the Honorable Commissioner For Patents:

This is an appeal to the Board of Patent Appeals and Interferences (the "Board") from the final rejection set forth in the Office Action mailed December 9, 2009.

In accordance with 37 C.F.R. § 41.31, Appellants electronically filed the Notice of Appeal via EFS-Web on February 8, 2010.

The present appeal is of pending claims 1-20.

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1. Real Party in Interest

The owner of the present patent application is Construction Research & Technology GmbH, by virtue of an assignment from the Appellants. Construction Research & Technology GmbH is a limited liability company organized under the laws of the country of Germany, and is a subsidiary of BASF SE, a corporation organized under the laws of the European Union. The assignment for this application was recorded in the records of the Assignment Division of the United States Patent and Trademark Office (the "Office" or "USPTO") on August 14, 2006 at Reel/Frame 018098/0150.

2. Related Appeals and Interferences

In accordance with 37 C.F.R. § 41.37(c)(1)(ii), Appellants hereby inform the Board that there are no other prior pending appeals, interferences, or judicial proceedings known to Appellants, Appellants' legal representative, or Assignee which may be related to, directly affect or be directly affected by, or have a bearing on the Board's decision in the pending appeal.

3. Status of Claims

The present application was given a 35 U.S.C. § 371 date of April 20, 2007 after being initially submitted to the Office on June 29, 2006 with original claims 1-21. A Final Office Action for this application was mailed by the Office on November 24, 2008. A Request for Continued Examination for this application was filed with the Office on February 23, 2009. A Final Office Action for this application, subsequent to Appellants' Request for Continued Examination, was mailed by the Office on December 9, 2009.

Claims 1-20 are currently under final rejection and constitute the claims on appeal.

In accordance with 37 C.F.R. § 41.37(viii), appealed claims 1-20 appear in the Claim Appendix below.

4. Status of Amendments

A Final Office Action was mailed by the Office on December 9, 2009.

No amendments to pending claims 1-20 have been filed with the Office subsequent to the mailing date of the Final Office Action.

5. Summary of Claimed Subject Matter

Independent claim 1 is directed to a settable mixture comprising: (i) a water absorbing composition; and (ii) an aqueous emulsion of organic polymer; or (iii) dispersible organic polymer, wherein the water absorbing composition (i) contains inorganic ingredients which are capable to react with water and the water absorbing composition (i) contains at least 13 weight % lime and at least 5 weight % of a cementitious composition of which components form ettringite during the absorption of water and wherein the amount of the aqueous emulsion of organic polymer (ii) in relation to (i) is such as to provide a ratio of combined weight of polymer solids to combined weight of ingredients which are capable to react with water of from 0.5 : 1 to 10: 1, and wherein the amount of dispersible organic polymer (iii) in relation to (i) is such as to give a ratio of combined weight of polymers to combined weight of ingredients which are capable to react with water of from 0.5 : 1 to 10: 1. Specification at page 2, paragraph 4, through page 5, paragraph 1.

Dependent claim 5 is directed to a settable mixture as described above with respect to claim 1, wherein in respect to the formation of ettringite the water absorbing composition (i) contains a stoichiometric surplus of lime. Specification at page 5, paragraph 6, first sentence.

Dependent claim 13 is directed to a settable mixture as described above with respect to claim 1, wherein the water absorbing composition (i) contains at least 62% lime. Specification at page 5, paragraph 2.

Dependent claim 14 is directed to a settable mixture as described above with respect to claim 1, wherein the sum of the weight of the lime and the weight of the cementitious composition is 67 of 100 of the total weight of the water absorbing composition (i), and wherein the water absorbing composition (i) contains at least 62% lime. Specification at page 4, paragraph 5 (as amended) and page 5, paragraph 2.

Dependent claim 16 is directed to a settable mixture as described above with respect to claim 1, wherein the sum of the weight of the lime and the weight of the cementitious composition is 67 of 100 of the total weight of the water absorbing composition (i), and wherein in respect to the formation of ettringite the water absorbing composition (i) contains a stoichiometric surplus of lime. Specification at page 4, paragraph 5 (as amended) and page 5, paragraph 6, first sentence.

6. Grounds of Rejection to be Reviewed on Appeal

A. The 35 U.S.C. § 103(a) rejection of claims 1-4, 6-12, 15 and 17-20 as being unpatentable over U.S. Patent Application Pub. No. 2002/0161071 to Mills, et al., in view of U.S. Patent No. 6,514,334 B1 to Perry, et al. Appellants wish to note that, while the rejection on page 2 of the final Office Action mailed December 9, 2009 lists claims 1-4, 6-12, 15 and 17-20, the summary on page 1 of the final Office Action and the discussion of the rejection at pages 2-4 refers to all of claims 1-20. Appellants therefore assume for the purposes of this Brief that all of claims 1-20 have been rejected.

7. Argument

Claims 1-4, 6-12, 15 and 17-20 have been rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent Application Pub. No. 2002/0161071 to Mills, et al. (“Mills”), in view of U.S. Patent No. 6,514,334 B1 to Perry, et al. (“Perry”). Appellants wish to note that, while the rejection on page 2 of the final Office Action mailed December 9, 2009 (the “Final Office Action”) lists claims 1-4, 6-12, 15 and 17-20, the summary on page 1 of the Final Office Action and the discussion of the rejection at pages 2-4 refers to all of claims 1-20. Appellants therefore assume for the purposes of this Brief that all of claims 1-20 have been rejected.

While the Office admits that Mills does not teach a composition which contains at least 13 weight % lime, the Office has alleged that Perry teaches a cementitious composition where lime may be present in amounts greater than 62 weight %. Preliminarily, Appellants respectfully submit that the Office has failed to consider the arguments presented in Appellants’ Response submitted August 8, 2008 and in Appellants’ Response submitted February 23, 2009 regarding the difference between “lime” and the convention of referring to calcium oxide as a constituent oxide of a distinct composition. These arguments were previously presented with regard to the difference between lime and the “lime content” of calcium aluminate, but apply equally to the differences between lime and the “calcium oxide content” of a cementitious composition.

As described in H.F.W. Taylor, Cement Chemistry, 2d, 1997, a copy of the pertinent portion of which is included as Appendix A, in the paragraph bridging pages 3 and 4, “[c]hemical formulae in cement chemistry are often expressed as sums of oxides; thus tricalcium silicate, Ca_3SiO_5 , can be written as $3\text{CaO}\cdot\text{SiO}_2$. This does not imply that the constituent oxides have a separate existence within the structure.” (emphasis added). This nomenclature is confirmed in Mills, at paragraph [0018].

Lime and calcium oxides which are constituent oxides of cementitious compositions are distinct compounds which react differently, and which must react differently in order to have their respective necessary effects on cementitious compositions, as required in the present application. The calcium oxide “content” of cementitious compositions is not available to react as lime, as it remains a part of the cementitious composition. If the lime “content” of a cementitious composition were to react as lime within the cementitious composition, there would

be no calcium left to form the clinker phases necessary for the cementitious composition to act as a hydraulic binder. Further, it is well known in the art that the various oxides that form many cements, such as calcium oxide, alumina, ferric oxide and silica, are, by themselves, rather unreactive with respect to water, and thus a mere mixture of these oxides would not work as a hydraulic binder. The cement manufacturing process is necessary to transform these oxides into a crystalline form which is suitable for reaction with water and can therefore react as a hydraulic binder.

For these reasons, the 80-99% CaO content of composition (B) of Perry is not free to react as lime, as recited by the claims currently under appeal. It is therefore clear that a person of skill in the art would not look to Perry for a teaching of free lime content to modify Mills as alleged by the Office. Appellants therefore respectfully submit that the Office has failed to state a prima facie case of obviousness with regard to the combination of Mills and Perry, and request that the Board require that the rejection of claims 1-20 be withdrawn.

Further, Appellants respectfully submit that Mills and Perry are not properly combinable in order to establish a prima facie case of obviousness. MPEP § 2141.03(VI) states that “[a] prior art reference must be considered in its entirety, i.e., as a whole, including portions that would teach away from the claimed invention. *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983), *cert. denied*, 469 U.S. 851 (1984)”. MPEP at 2100-126 (emphasis in original). Further, MPEP § 2143.01(V) states that, “[i]f proposed modification would render the prior art invention being modified unsatisfactory for its intended purpose, then there is no suggestion or motivation to make the proposed modification. *In re Gordon*, 733 F.2d 900, 221 USPQ 1125 (Fed. Cir. 1984)”. MPEP at 2100-140.

The present specification discloses that, in order to achieve the desired high early strength provided by the presently claimed settable mixture, formation of Ettringite is necessary. At page 4, lines 22-26 (as amended), it is stated that “Ettringite is a calcium trisulphoaluminate having 32 molecules of water of crystallization and has the formula $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$. Ettringite is produced by the hydration of cementitious materials containing calcium aluminate

and **calcium sulphate**” (emphasis added). Mills contains a similar disclosure. Therefore, in order for the present settable mixture, as well as that of Mills, to be suitable for their intended purposes, the composition must contain calcium sulphate.

Perry does not disclose the use of calcium sulphate, and the composition of Perry cannot form Ettringite. Thus, if the composition of Perry, taken as a whole, were to be combined with Mills, the resulting composition would not contain calcium sulphate, as this component is absent in Perry, and therefore could not form Ettringite. The composition would not be able to obtain a high early strength. For these reasons, combining Perry with Mills renders Mills unsatisfactory for its intended purpose, and there is no suggestion or motivation to modify Mills according to Perry in order to increase the lime content of the Mills composition.

Furthermore, Mills discloses a maximum amount of 10% by weight of lime. *See* Abstract, paragraph [0010]. For this reason, there is no motivation in Mills to increase the amount of lime according to the teaching of Perry, as alleged by the Office.

Also for the above reasons, a person of skill in the art would not look to Perry for ways to modify Mills in order to obtain an even earlier high strength cementitious composition than that disclosed in Mills. Mills makes no disclosure of how Ettringite enables high early strength, while the present specification shows that additional lime will provide a settable composition with an even earlier high strength than that of Mills. Perry provides no motivation to reduce the time needed for Ettringite formation by adding excess lime, because Perry does not contain the components necessary to form Ettringite. For all of these reasons, the Office has not established a prima facie case of obviousness.

Appellants submit that, since claim 1 is not taught or suggested by the combination of Mills and Perry, for the above reasons, claims 2-20, which depend from claim 1, are also not taught or suggested. *See In re Fine*, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988). (“If an independent claim is nonobvious under 35 U.S.C. 103, then any claim depending therefrom is nonobvious.” MPEP § 2143.03 at page 2100-142.)

Specifically with regard to claims 5 and 16, the Office admits, at page 3 of the Final Office Action, that “Mills et al. does not teach that the water absorbing composition contains a

stoichiometric surplus of lime, i.e., an amount of lime that is not included in the ettringite forming reaction.” The Office alleges, however, that “Perry et al. teaches adding up to 30 weight percent hydrated lime to the cementitious mixture comprising compositions A and B. Adding this lime after the composition has been formed would preclude it from participating in the reaction.” Appellants respectfully submit that this assertion is technically incorrect.

Claims 5 and 16 of the present application are directed to compositions of claim 1 or claim 2, “wherein in respect to the formation of ettringite the water absorbing composition (i) contains a stoichiometric surplus of lime.”

Perry discloses a process for making a cementitious mixture which includes mixing granular components A and B (Abstract). The Office alleges that the reaction of components A and B will be complete once components A and B are mixed. This is not true. Components A and B, when mixed, form a “homogenous cementitious mixture” (col. 6, lines 40-41). However, as is well known in the art of cementitious compositions, components A and B will not react until water is added to the homogenous mixture. Therefore, the addition of up to 30 weight percent lime (col. 6, lines 44-45) does not teach a stoichiometric surplus in any sense, because the reaction has not yet begun and the required amount for reaction not indicated, when the lime is added to the homogenous mixture of Perry.

For these reasons, Perry gives no indication that any additional lime added to the cementitious mixture of Perry is more than what will be required or consumed in the cementitious reaction that will occur once water is added to the cementitious mixture of Perry. Further, Perry makes no mention of providing lime at a stoichiometric surplus, or that there is any desire to increase the speed of the reaction of components A and B once water is added to the cementitious mixture. Therefore, there is no teaching, suggestion, or motivation in Perry to add a stoichiometric surplus of lime to the cementitious mixtures of Mills and/or Perry.

For this reason, Appellants respectfully submit that the combination of Mills and Perry fails to teach or suggest the subject matter of claims 5 and/or 16 of the present application.

Specifically with regard to claims 13 and 14, the Office alleges, at page 2 of the Final Office Action with regard to Perry, that “assuming that composition B is made of 90% lime, lime would be in the composition in an amount greater than 62 weight %”.

Claims 13 and 14 of the present application are directed to compositions of claim 1 or claim 2, “wherein the water absorbing composition (i) contains at least 62 weight % lime.”

As discussed above, the alleged “lime” of composition B, being part of a complex oxide structure and not having a separate existence within the structure, is not free to react as lime reacts in the present application. Perry discloses a maximum amount of 30 weight percent lime (col. 6, line 45). Therefore, the combination of Mills and Perry fails to teach or suggest the subject matter of claims 13 and/or 14 of the present application.

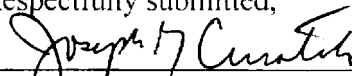
For all of the above reasons, Appellants respectfully request that the Board require that the rejection of claims 1-20 be withdrawn.

Conclusion

Appellants have addressed the instant rejections presented in the Final Office Action with respect to independent claim 1 and dependent claims 5, 13, 14 and 16 in particular, and have distinguished the applied references as discussed above. It is therefore deemed unnecessary to address the Office’s specific allegations regarding the remaining dependent claims. Appellants therefore traverse these allegations, and do not concur with the same either explicitly or implicitly by not refuting each individually.

Appellants submit that the remarks presented hereinabove overcome all the existing 35 U.S.C. § 103(a) rejections of all pending claims. Appellants respectfully request the Board to reverse the final rejections of these claims, and to require the Office to issue a formal notice of allowability of claims 1-20 over the art of record.

Respectfully submitted,



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Date: April 8, 2010

8. Claims Appendix

In accordance with 37 C.F.R. § 41.37 (c)(1)(ix), the claims on appeal are as follows:

1. (Previously Presented) A settable mixture comprising
 - (i) a water absorbing composition and
 - (ii) an aqueous emulsion of organic polymer or
 - (iii) dispersible organic polymer,wherein the water absorbing composition (i) contains inorganic ingredients which are capable to react with water and the water absorbing composition (i) contains at least 13 weight % lime and at least 5 weight % of a cementitious composition of which components form ettringite during the absorption of water and wherein the amount of the aqueous emulsion of organic polymer (ii) in relation to (i) is such as to provide a ratio of combined weight of polymer solids to combined weight of ingredients which are capable to react with water of from 0.5 : 1 to 10: 1, and wherein the amount of dispersible organic polymer (iii) in relation to (i) is such as to give a ratio of combined weight of polymers to combined weight of ingredients which are capable to react with water of from 0.5 : 1 to 10: 1.
2. (Previously Presented) A settable mixture according to claim 1, wherein the sum of the weight of the lime and the weight of the cementitious composition is 67 to 100 of the total weight of the water absorbing composition (i).
3. (Previously Presented) A settable mixture according to claim 1, wherein the water absorbing composition (i) contains at least 25 weight % lime.
4. (Previously Presented) A settable mixture according to claim 1, wherein the cementitious composition contains calcium aluminate and calcium sulfate.
5. (Previously Presented) A settable mixture according to claim 1, wherein in respect to the formation of ettringite the water absorbing composition (i) contains a stoichiometric surplus of lime.

6. (Previously Presented) A method of applying a coating to a surface which method comprises forming a settable mixture according to claim 1, containing a water absorbing composition (i) and an aqueous emulsion of organic polymer (ii) and putting the settable mixture on the surface to form a coating.
7. (Previously Presented) A method of applying a coating to a surface which method comprises forming a settable mixture according to claim 1, containing water absorbing composition (i) and dispersible organic polymer (iii), combining the settable mixture with water and putting the mixture on the surface to form a coating.
8. (Previously Presented) The coating made according to the method which is defined in claim 6.
9. (Previously Presented) A method of applying a coating to a surface which method comprises forming a settable mixture according to claim 1, containing a water absorbing composition (i) and an aqueous emulsion of organic polymer (ii) and putting the settable mixture on the surface to form a coating, wherein the coating comprises a rock support means.
10. (Previously Presented) A method of applying a coating to a surface which method comprises forming a settable mixture according to claim 1, containing a water absorbing composition (i) and an aqueous emulsion of organic polymer (ii) and putting the settable mixture on the surface to form a coating, wherein the coating comprises a waterproofing means.
11. (Previously Presented) The settable mixture according to claim 1 wherein the amount of the aqueous emulsion of organic polymer (ii) in relation to (i) is such as to provide a ratio of combined weight of polymer solids to combined weight of ingredients which are capable to react with water of from 1: 1 to 4: 1.

12. (Previously Presented) The settable mixture according to claim 1 wherein the amount of dispersible organic polymer (iii) in relation to (i) is such as to give a ratio of combined weight of polymers to combined weight of ingredients which are capable to react with water of from 1: 1 to 4: 1.
13. (Previously Presented) The settable mixture according to claim 1 wherein the water absorbing composition (i) contains at least 62 weight % lime.
14. (Previously Presented) The settable mixture according to claim 2 wherein the water absorbing composition (i) contains at least 62 weight % lime.
15. (Previously Presented) The settable mixture according to claim 2 wherein the cementitious composition contains calcium aluminate and calcium sulfate.
16. (Previously Presented) The settable mixture according to claim 2 wherein in respect to the formation of ettringite the water absorbing composition (i) contains a stoichiometric surplus of lime.
17. (Previously Presented) The method of applying a coating to a surface according to claim 6 wherein the coating is at least 2 mm in thickness.
18. (Previously Presented) The method of applying a coating to a surface according to claim 7 wherein the coating is at least 2 mm in thickness.
19. (Previously Presented) The coating made according to the method which is defined in claim 7.
20. (Previously Presented) A method of applying a coating to a surface which method comprises forming a settable mixture according to claim 1, containing water absorbing composition (i) and dispersible organic polymer (iii), combining the settable mixture with water and putting the mixture on the surface to form a coating, wherein the coating comprises a rock support means or a waterproofing means.

9. Evidence Appendix


Appendix A: Taylor, H.F.W., Cement Chemistry. 2nd Edition, Thomas Telford Publishing, 1997, pages 1-5.

APPENDIX A

Cement chemistry

2nd edition

H.F.W. Taylor
Emeritus Professor of Inorganic Chemistry
University of Aberdeen

 Thomas Telford

Preface

The previous edition of this book, published by Academic Press in 1990, is both out of print and out of date, and when Thomas Telford invited me to prepare a new edition I was delighted to comply. I am most grateful both to them and to Academic Press, whose release of the copyright made the present edition possible.

This book deals with the chemistry of the principal silicate and aluminate cements used in building and civil engineering. It is directed primarily to those whose background is in chemistry, materials science or related disciplines. Emphasis is placed throughout on the underlying science rather than on practical applications, which are well covered in other works. The cements considered fall into the category of hydraulic cements: they set and harden as a result of chemical reactions with water, and if mixed with water in appropriate proportions continue to harden even if subsequently placed in water. Much the most important is Portland cement. Chapters 1 to 4 deal mainly with the chemistry of Portland cement manufacture and the nature of the resulting product. Chapters 5 to 8 deal mainly with the processes that occur when this product is mixed with water and with the nature of the hardened material. Chapters 9 to 11 deal with the chemistry of other types of cement, of admixtures for concrete and of special uses for cements. Chapter 12 deals with chemical and micro-structural aspects of concrete, including ones that affect its durability or limit its service life.

The literature of cement chemistry is voluminous; the abstracting journal, *Cementis Research Progress*, has for some years listed around 1000 new contributions annually. The output of the seven years since the previous edition of this book appeared is reflected in the increased number of references to the literature, which is approximately 1500 compared with 1300 in that edition. Of necessity, coverage in the present book has been selective, but it is hoped that the most important contributions up to mid-1996 have been covered. The advances in some parts of the subject have been greater than in others, and this is reflected in the differences between this and the previous edition; some sections have been totally rewritten whereas others have changed relatively little.

As one who has seen the subject develop over a period of nearly 50 years, I am highly aware of the problems that those entering the subject

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Cement Chemistry

Appendix: Calculated X-ray powder diffraction patterns for
tricalcium silicate and clinker phases

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1 Portland cement and its major constituent phases

1.1 Introduction

1.1.1 Portland cement: general

Portland cement is made by heating a mixture of limestone and clay, or other materials of similar bulk composition and sufficient reactivity, ultimately to a temperature of about 1450°C. Partial fusion occurs, and nodules of clinker are produced. The clinker is mixed with a few per cent of calcium sulfate and finely ground, to make the cement. The calcium sulfate controls the rate of set and influences the rate of strength development. It is commonly described as gypsum, but this may be partly or wholly replaced by other forms of calcium sulfate. Some specifications allow the addition of other materials at the grinding stage. The clinker typically has a composition in the region of 67% CaO, 22% SiO₂, 5% Al₂O₃, 3% Fe₂O₃ and 3% other components, and normally contains four major phases, called alite, belite, aluminite and ferrite. Several other phases, such as alkali sulfates and calcium oxide, are normally present in minor amounts. Hardening results from reactions between the major phases and water.

Alite is the most important constituent of all normal Portland cement clinkers, of which it constitutes 50–70%. It is tricalcium silicate (Ca₃SiO₄) modified in composition and crystal structure by ionic substitutions. It reacts relatively quickly with water, and in normal Portland cement is the most important of the constituent phases for strength development; at ages up to 28 days, it is by far the most important.

Belite constitutes 15–30% of normal Portland cement clinkers. It is dicalcium silicate (Ca₂SiO₄) modified by ionic substitutions and normally present wholly or largely as the β polymorph. It reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. By one year, the strengths obtainable from pure alite and pure belite are about the same under comparable conditions.

Aluminite constitutes 5–10% of most normal Portland cement clinkers. It is tricalcium aluminite (Ca₃Al₂O₆), substantially modified in composition and sometimes also in structure by ionic substitutions.

Cement chemistry

It reacts rapidly with water, and can cause undesirably rapid setting unless a set-controlling agent, usually gypsum, is added.

Ferrite makes up 5-15% of normal Portland cement clinkers. It is tetra-calcium aluminoferrite ($\text{Ca}_2\text{Al}_2\text{FeO}_5$), substantially modified in composition by variation in Al/Fe ratio and ionic substitutions. The rate at which it reacts with water appears to be somewhat variable, perhaps due to differences in composition or other characteristics, but in general is high initially and low or very low at later ages.

1.1.2 Types of Portland cement

The great majority of Portland cements made throughout the world are designed for general constructional use. The standard specifications with which such cements must comply are similar, but not identical, in all countries and various names are used to define the material, such as Class 42.5 Portland cement in current European and British standards (42.5 is the minimum 28-day compressive strength in MPa), Types I and II Portland cement in the ASTM (American Society for Testing and Materials) specifications used in the USA, or Ordinary Portland Cement (OPC) in former British standards. Throughout this book, the term 'ordinary' Portland cements is used to distinguish such general-purpose cements from other types of Portland cement, which are made in smaller quantities for special purposes.

Standard specifications are, in general, based partly on chemical composition or physical properties such as specific surface area, and partly on performance tests, such as setting time or compressive strength developed under standard conditions. The content of MgO^* is usually limited to 4-5%, because quantities of this component in excess of about 2% can occur as periclase (magnesium oxide), which through slow reaction with water can cause destructive expansion of hardened concrete. Free lime (calcium oxide) can behave similarly. Excessive contents of SO_3 can also cause expansion, and upper limits, typically 3-5% for ordinary Portland cements, are usually imposed. Alkalis (K_2O and Na_2O) can undergo expansive reactions with certain aggregates, and some specifications limit the content, e.g. to 0.6% equivalent Na_2O ($\text{Na}_2\text{O} + 0.66 \text{K}_2\text{O}$). Other upper limits of composition widely used in specifications relate to matter insoluble in dilute acid, and loss on ignition. Many other minor components are limited in content by their effects on the manufacturing process, or the properties, or both, and in some cases the limits are defined in specifications.

Rapid-hardening Portland cements have been produced in various ways, such as varying the composition to increase the alite content, finer grinding of the clinker, and improvements in the manufacturing process,

* Confusion can arise because the names or formulae of compounds can be used to denote either phases or components; this applies especially to CaO and MgO . Here and elsewhere, chemical or mineral names of oxides (e.g. calcium oxide, magnesium oxide, lime, periclase) will generally be used for phases, and formulae (e.g. CaO , MgO) for components. Mineral names or prebated formulae (e.g. $n\text{-Al}_2\text{O}_3$) are never used for components.

Portland cement and its major constituent phases

e.g. finer grinding or better mixing of the raw materials. The alite contents of Portland cements have increased steadily over the one and a half centuries during which the latter have been produced, and many cements that would be considered ordinary today would have been described as rapid hardening only a few decades ago. In the ASTM specifications, rapid-hardening Portland cements are called high early strength or Type III cements. For both ordinary and rapid-hardening cements, both lower and upper limits may be imposed on strengths at 28 days, upper limits being a safeguard against poor durability resulting from the use of inadequate cement contents in concrete.

Destructive expansion from reaction with sulfates can occur not only if the latter are present in excessive proportion in the cement, but also from attack on concrete by sulfate solutions. The reaction involves the Al_2O_3 -containing phases in the hardened cement, and in sulfate-resisting Portland cements its effects are reduced by decreasing the proportion of the aluminate phase, sometimes to zero. This is achieved by decreasing the ratio of Al_2O_3 to Fe_2O_3 in the raw materials. In the USA, sulfate-resisting Portland cements are called Type V cements.

White Portland cements are made by increasing the ratio of Al_2O_3 to Fe_2O_3 , and thus represent the opposite extreme in composition to sulfate-resisting Portland cements. The normal, dark colour of Portland cement is due to the ferrite, formation of which in a white cement must thus be avoided. It is impracticable to employ raw materials that are completely free from Fe_2O_3 and other components, such as Mn_2O_3 , that contribute to the colour. The effects of these components are therefore usually minimized by producing the clinker under slightly reducing conditions and by rapid quenching. In addition to alite, belite and aluminate, some glass may be formed.

The reaction of Portland cement with water is exothermic, and while this can be an advantage under some conditions because it accelerates hardening, it is a disadvantage under others, such as in the construction of large dams or in the lining of oil wells, when a cement slurry has to be pumped over a large distance under pressure and sometimes at a high temperature. Slower heat evolution can be achieved by coarser grinding, and decreased total heat evolution by lowering the contents of alite and aluminate. The ASTM specifications include definitions of a Type II or 'moderate heat of hardening' cement, and a more extreme Type IV or 'low heat' cement. The Type II cement is also suitable for conditions exposed to moderate sulfate attack, and is widely used in general construction work. Heat evolution can also be decreased by partially replacing the cement by flyash (pulverized fuel ash; pfa) or other materials (Chapter 9), and this is today a widely used solution. The specialized requirements of oil well cements are discussed in Section 11.8.

1.1.3 Cement chemical nomenclature and other abbreviations

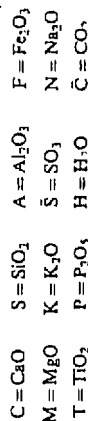
Chemical formulae in cement chemistry are often expressed as sums of oxides; thus tricalcium silicate, Ca_3SiO_5 , can be written as $3\text{CaO} \cdot \text{SiO}_2$. This does not imply that the constituent oxides have any separate

Cement chemistry

existence within the structure. It is usual to abbreviate the formulae of the commoner oxides to single letters, such as C for CaO or S for SiO₂. Ca₃SiO₅ thus becoming C₃S. This system is often combined with orthodox chemical notation within a chemical equation, e.g.



or even within a single formula, as in C₁₁A₇·CaF₂ for Ca₁₁Al₇O₃₂F₂. The abbreviations most widely used are as follows.



The formulae of the simple oxide phases (e.g. CaO) are usually written in full. Other abbreviations and units used in this book are as follows.

1.1.3.1 Techniques

BEI = backscattered electron imaging. BSE = backscattered electron. DTA = differential thermal analysis. EPMA = electron probe microanalysis. ESCA = electron spectroscopy for chemical analysis (X-ray photoelectron spectroscopy). GLC = gas-liquid chromatography. GPC = gel permeation chromatography. IR = infrared. MIP = mercury intrusion porosimetry. NMR = nuclear magnetic resonance. QXDA = quantitative X-ray diffraction analysis. SEM = scanning electron microscope (c,y). STEM = scanning transmission electron microscope (c,y). TEM = transmission electron microscope (c,y). TG = thermogravimetry. TMS = trimethylsilylation). XRD = X-ray diffraction. XRF = X-ray fluorescence.

1.1.3.2 Materials

C-S-H = poorly crystalline or amorphous calcium silicate hydrate of unspecified composition. Ggbs = ground granulated blastfurnace slag. Hcp = hardened cement paste. Pla = pulverized fuel ash (flyash).

1.1.3.3 Properties or reactions

AR = alumina ratio (alumina modulus). ASR = alkali silica reaction. DEF = delayed ettringite formation. LSF = lime saturation factor. SR = silica ratio (silica modulus). C_x = analytical (total) concentration of x, irrespective of species [x] = concentration of species x. {x} = activity of species x. RH = relative humidity. Na₂O_e = equivalent Na₂O (mass % Na₂O + 0.66 K₂O). (+)2V, (-)2V, optic sign and optic axial angle.

1.1.3.4 Pressure units

1 MPa = 1 Nmm⁻² = 10 bar = 9.87 atm = 7500 torr = 145.0 lb in⁻² = 10.198 kg cm⁻².

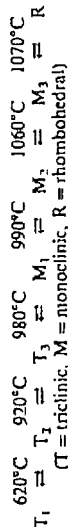
1.2 Alite

1.2.1 Polymorphism and crystal structure

On being heated, pure C₃S undergoes a series of reversible phase transitions, which have been detected by a combination of DTA,

Portland cement and its major constituent phases

high-temperature XRD and high-temperature light microscopy (B1,G1, M1-M5,R1,R2,Y1):



The pure compound, when cooled to room temperature, is thus T₁. In production clinkers, due to the incorporation of substituent ions, the form present at room temperature normally approximates to M₁ or M₃ or a mixture of these; rarely, T₁ is found (M1-M5,T1). There has been some uncertainty as to the number and nomenclature of these polymorphs; reported M_{1a} and M_{2a} forms appear to be identical with M₁, leaving reported M_{1a} and M_{2a} forms to be called simply M₁ and M₂ respectively (M4,M5).

Jeffery (J1) made the first determination of the crystal structure. He showed that the forms now known as R, T₁ and M₃ had closely similar structures, and determined the approximate or pseudostructure common to all three; it was built from Ca²⁺, SiO₄⁴⁻ and O²⁻ ions, the last being bonded only to six Ca²⁺ ions, as in CaO. Later, more exact determinations were reported for T₁ (G2), M₃ stabilized by Mg²⁺ (N1), M₃ with increased disorder isolated from a works clinker (M6), R at 1200°C (N2) and R stabilized with S²⁻ (I1). Figure 1.1 shows the structure of the R form. The known structures are all closely similar as regards the positions of the Ca²⁺ and O²⁻ ions and of the Si atoms, but differ markedly in the orientations of the SiO₄⁴⁻ tetrahedra, which show varying degrees of disorder.

The structural differences between the polymorphs affect the coordination of the Ca²⁺ ions and the O atoms of the SiO₄⁴⁻ tetrahedra. For each polymorph, there are several crystallographically distinct Ca sites, having different coordination, and for a given site, the coordination sometimes varies between individual atoms due to orientational disorder in the surrounding SiO₄ tetrahedra. Definitions of the Ca coordination numbers are somewhat arbitrary due to variations in the lengths of the bonds: e.g. in the R form at 1200°C, the Ca atoms in one of the sites could be regarded as 7 coordinated if bonds as long as 0.296 nm are counted, and 5 coordinated if they are not (N2). If such abnormally long bonds are excluded, the mean coordination number of the Ca is 5.66 in the R polymorph, 6.15 in M₃ and 6.21 in T₁ (M5). In relation to reactivity towards water, the coordination of the oxygen atoms is possibly more important than that of Ca. This has not been discussed in detail in the literature, but mean oxygen coordination numbers may be expected to increase with those of calcium.

Table 1.1 gives the crystal data for the C₃S polymorphs that have been obtained using single-crystal methods. The literature contains additional unit-cell data, based only on powder diffraction evidence. Some of these may be equivalent to ones in Table 1.1, since the unit cell of a monoclinic or triclinic crystal can be defined in different ways, but some are certainly incorrect. Because only the stronger reflections are recorded, and for

10. Related Proceedings Appendix

None.